

# A DENDRITIC PROCESS FOR THE CATALYTIC REDUCTION OF HEAVY OILS, KEROGENS, PLASTICS, BIO-MASSSES, SLUDGES AND ORGANIC WASTES TO LIGHT HYDROCARBON LIQUIDS, CARBON DIOXIDE AND AMINES

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## REFERENCE TO RELATED APPLICATIONS

This application claims an invention which was disclosed in Provisional Application Number 60/277,087, filed March 19, 2001, entitled "A PROCESS FOR THE CATALYTIC REDUCTION OF HEAVY OILS, KEROGENS, PLASTICS, BIO-MASSSES, SLUDGES AND ORGANIC WASTE TO LIGHT HYDROCARBON LIQUIDS, CARBON DIOXIDE AND AMINES". The benefit under 35 U.S.C. § 119(e) of the United States provisional application is hereby claimed, and the aforementioned application is hereby incorporated herein by reference.

## BACKGROUND OF THE INVENTION

### FIELD OF THE INVENTION

The invention pertains to the field of organic chemistry. More particularly, the invention pertains to a dendritic process for the catalytic reduction of organic compositions.

### DESCRIPTION OF RELATED ART

The three states of matter are solids, liquids and gases. Depending on pressure and temperature, the three phases can exist singly or in equilibrium with other phases. Water has what is known as three "co-existence curves," consisting of a solid-gas equilibrium (called the sublimation curve), a liquid-gas equilibrium (called the vapor pressure curve), and a solid-liquid equilibrium (called the melting curve). There also exists a "triple point," at which all three phases exist in equilibrium. The point on the vapor pressure curve where the liquid and vapor concentration become identical is called the critical point. The temperature at this point is called the "critical temperature" (*e.g.*,  $T_c$  water = 374° C) and the pressure is called the "critical pressure" (*e.g.*,  $P_c$  water = 218 atmospheres). *See, e.g.*, O. Maass and E.W.R Steacie, An Introduction to the Principles of Physical Chemistry (1939), pages 80-83, John Wiley and Sons, Inc.; *see* <http://www.kobelco.co.jp/p108/p14/sfe01.htm>.

No gas can be liquefied above its  $T_c$ . For example, as water is heated under pressure, it slowly begins to lose its H-bonding characteristics, behaves more and more like a lower dielectric constant solvent, and becomes less dense. Super-critical water is the fluid that is formed when water is heated above its  $T_c$ . The density of super critical water can continuously be controlled between gas-like and liquid-like values, by varying pressure and temperature. Thus, super-critical water can have a dielectric constant between 5 to 25, depending on conditions. This corresponds to the dielectric properties of polar organic liquids under normal conditions. This property partially explains the ability of super-critical water to dissolve nonpolar organic compounds. Above its  $T_c/P_c$ , super-critical water (hereinafter referred to as "SCW") has a dielectric constant of less than 5 and a density of 0.2 gm/ml. Hence, as a super-critical fluid, SCW simultaneously behaves both as a liquid and a gas, with the solvent power of an organic liquid, such as benzene.

The major constituents of 1) biosynthetic molecules, such as those of plant and/or animal tissue, and 2) geological and/or man-made polymers are: carbohydrates, lignin, waxes, lipids, proteins, kerogens, mineral oils and plastics. It is known in the prior art that classic organic reactions involving these constituents, such as hydrolysis, bond cleavage and bond formation, occur in the sub-critical zone, as described in U.S. Patent No. 4,515,713, and at or above the super-critical temperature of water. *See, e.g., Kuhlmann et al., J. Org. Chem.* 59: 3098-3101 (1994); C.R. Strauss, *Aust. J. Chem.* 52: 83-96 (1999). For example, hydrolysis of esters, thioesters and amides occurs in SCW, and is usually accompanied by decarboxylation. *See, e.g., U.S. Patents No. 5,344,975, No. 5,329,054, and No. 5,630,854, which teach the use of acidic, basic and neutral catalysts, respectively, in such reactions.*

It is further known in the prior art that carbon-carbon and carbon-sulfur bond rupture, followed by hydrogenation of the terminal ionic or free radical end, occur via processes such as thermal hydrocracking (*see, e.g., Gray et al., Energy and Fuels* 6(4): 478-485 (1992)) and/or hydro-desulfurization (*see, e.g., Whitehurst et al., Adv. Catal.* 42: 345 (1998)). Pyrolysis without further hydrogenation generates coke; examples of coking found in the prior art include thermal generation of methane gas, distillates and coke, during pyrolyzation of coal and wood (an excellent reference is found at <http://www.newcastle.edu.au>). The array of products so generated typically is separated by well known methods, such as, for example, capture of gases, condensation of liquids in a distillation tower, and crystallization and/or precipitation of solids. Well known examples of capture of gases are precipitation of carbon dioxide by lime, formation of amine salts by acids, and condensation of low boiling hydrocarbons by cryogenic means. A well known

example of a distillation tower partitioning is the separation of gases and liquids of differing boiling points from each other. Table 1, below, presents an example of hydrocarbon boiling ranges for a distillation tower.

5                    **Table 1:**

<b><u>Carbon Chain Length</u></b>	<b><u>Class</u></b>	<b><u>Boiling Point Range (° C)</u></b>
C5–C10	Gasoline	37-175
C10–C15	Kerosene/Jet Fuel	175-275
C12-C20	Diesel	190-330
C14-C22	Fuel Oil	230-360
C20–C30	Lubricating Oil	> 350
C22-C40	Petroleum Jelly	40-60 (m. pt.)
C25-C50	Paraffin Wax	50-65 (m. pt.)
C50 + poly cyclics	Tar/bitumen	> 400

It is known in the prior art that aqueous glycerol solutions are insoluble in hydrocarbons. *See, e.g., Merck Index Entry 4493 ISBN # 0911910-1-2-3 (1996).* Further, U.S. Patent No. 4,478,612 teaches the use of glycerol as a water-binding astringent in supercritical carbon dioxide.

The term "dendritic process" is intended herein to refer to a process comprising a simultaneous set of multi-stepped reactions, and the separation and isolation of purified streams of targeted variable products from raw material constituents in a single stage reaction vessel. Examples of such are found in, *e.g., Canadian Patent No. 2,249,110; C.R. Strauss, Aust. J. Chem. 52: 83-96 (1999); and J. Haggin, Chemical and Engineering News 74 (23): 38 (1999), the complete disclosures of which are hereby incorporated herein by reference.*

An ideal dendritic process is described by Paul A Wender, *ACS Chemical & Engineering News*, January 8 2001, page 27, the complete disclosure of which is hereby incorporated herein by reference. The ideal dendritic process has: 1) the capability to use readily available, low cost, mixed raw materials from diverse sources; 2) a short cycle time; 3) a net positive energy balance; 4) no requirement for an organic solvent; 5) robust process variables and: a) is multi-stepped in one reaction vessel; b) leaves no environmental footprint; and c) generates controllable purified separated products in 100% yields, while involving as few personnel and as little equipment as possible.

### SUMMARY OF THE INVENTION

The present invention pertains to a process for the catalytic reduction of heavy oils, kerogens, plastics, bio-masses, sludges and organic wastes to light hydrocarbon liquids, carbon dioxide and amines, all in a single reaction vessel. Disclosed herein are multiple examples of an improved dendritic process for the reaction of variegate raw materials, and the separation and isolation of the products formed thereby. The invention takes advantage of the reduction in the number of profligate process steps, the cycle time for the reactions, and the capacity to separate the products using a dendritic process. The invention thus directly addresses the need in the art for an improved dendritic process, which is suitable for application in the processing and recycling or disposal of waste from numerous and variable sources, such as, for example, agricultural, industrial and municipal waste products, and including, but not limited to, various wastes that are toxic or potentially hazardous to human or animal health or the environment.

In one embodiment, a mixture of synthetic polymers comprising nylon 6, nylon 6,6, nylon 6,10 and nylon 6,12 is subjected to a high temperature in the presence of SCW, thereby producing a mixture of  $\omega$ -amino caproic acid, 1,6-diamino hexane, hexan-1,6-dioic acid, decan-1,10-dioic acid, and dodecan-1,12-dioic acid. Decarboxylation of the amino acid and the diacids generate fractionally distillable carbon dioxide, plus pentyl amine, 1,6-diamino hexane, butane, octane, and decane. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. Hence, in one reaction vessel, water is consumed and a mixture of four nylon polymers generates two amines, three hydrocarbons and carbon dioxide.

In another embodiment, polyethylene is subjected to a high temperature in the presence of water and iron oxide embedded in an alumina-silica matrix or a basic catalyst, such as sulfide. Reductive thermolytic cleavage of carbon-carbon bonds and oxidation of

the sulfide to sulfate ion yields  $C_{22}$  to  $C_{40}$  waxes or fractionally distillable  $C_{10}$  to  $C_{22}$  hydrocarbons, respectively. Hence, in one reaction vessel, water is consumed and a mixture of hydrocarbons is formed.

In an yet another embodiment, a mixture of variegate source triglycerides and lipids (preferably with some protein "contaminant") of animal and/or vegetable origin is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids; hydrolysis of the triglycerides and lipids produces a mixture of  $C_4$  to  $C_{24}$  carboxylic acids, plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, and  $C_3$  to  $C_{23}$  hydrocarbons. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. Also optionally, glycerol is added as a desiccant for the generated hydrocarbons and absorbent for the amines. Thus, the dry hydrocarbon phase optionally is separated before fractional distillation is carried out. Hence, in one reaction vessel, water is consumed and a mixture of triglycerides, lipids, and protein is converted to amines, desiccated hydrocarbons, glycerol and carbon dioxide.

In still another embodiment, animal excrement and vegetable wastes that have a fair proportion of triglycerides, lipids and protein, is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids; hydrolysis of the triglycerides and lipids produces a mixture of  $C_4$  to  $C_{24}$  carboxylic acids, plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, and  $C_3$  to  $C_{23}$  hydrocarbons, with little, if any, methane gas. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. A higher proportion of protein generates a higher ratio of amines to hydrocarbons. Capture and isolation of the putrid smelling amines provides an odor-free process and nitrogen reduced residue. Solid insoluble coke residue (cellulose derived) and mineral salts also are obtained. Hence, in one reaction vessel, water is consumed and human, swine, or bovine excrement and plant matter are converted to carbon dioxide, amines, hydrocarbons, glycerol, and nitrogen-depleted carbonaceous compost. This odor and pathogen-free residue is suitable for use as a low-grade fuel or compost.

In an additional embodiment, Lake Asphalt Tar Sand that has a fair proportion of carboxylic acids is subjected to a high temperature in the presence of super-critical water.



Inherent clay catalyst causes decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons, generating fractionally distillable  $C_{12}$ , plus other hydrocarbons. Solid insoluble residue (mineral salts), and very heavy organo-sulfur contaminated tars also are obtained. Hence, in one reaction vessel, water is consumed and tar sand is converted to carbon dioxide, hydrocarbons, and residual tar-contaminated clay.

In yet an additional embodiment, heavy oils that have a fair proportion of carboxylic acids are subjected to a high temperature in the presence of SCW, with an iron oxide catalyst or amino acid catalyst, causing decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons. Fractionally distillable  $C_{13}$  to  $C_{30}$  hydrocarbons is generated. Optionally, the use of ash residue from Lake Asphalt Tar Sand as catalyst in the reductive generation of lighter oils from heavy crude causes the separation of metal contaminants and organo-sulfur compounds from the lighter fractions. Solid insoluble residue (mineral salts) containing very heavy tars and organo-sulfur compounds also are obtained. Hence, in one reaction vessel, water is consumed and heavy oil is converted to carbon dioxide, hydrocarbons, and residual tar contaminated clay (in the case of alumina-silica-iron oxide catalyst) or organo-sulfur tar contaminant residual V-Ni-Fe metals (in the case of amino acid catalyst).

In still an additional embodiment, heavy oils supplemented with waste fats and lipids (as a processing aid in the pipeline transport of crude) are subjected to a high temperature in the presence of SCW. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons thus generates fractionally distillable desiccated lighter hydrocarbons, physically separable water-loaded glycerol, and filterable solids. The solid insoluble residue contains mineral salts and very heavy tars. Hence, in one reaction vessel, water is consumed and lipid-supplemented heavy oil is converted to carbon dioxide, hydrocarbons, and residual organo-sulfur tar contaminant metals.

In a further embodiment, Albert shale from Stoney Creek, New Brunswick is subjected to a high temperature in the presence of SCW. Reductive thermolytic cleavage of carbon-carbon bonds yields  $C_{12}$  to  $C_{26}$  hydrocarbons, as determined by GC/MS.

In yet a further embodiment, extracted lignin or black liquor from the Kraft (sulfide plus carbonate) and Soda-AQ (carbonate) process are subjected to super-critical temperatures. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons generates fractionally distillable hydrocarbons and physically separable precipitated carbonaceous solids. The separated

aqueous fraction from the Kraft process contains a mixture of carbonate and sulfate ion, but no substantial sulfide ion. Hence, in one reaction vessel, water is consumed and pulp black liquor is converted to carbon dioxide, hydrocarbons, carbonaceous fuel and green liquor, without resorting to an energy intensive five stage evaporation in order to concentrate the black liquor. This makes the environmentally more friendly Soda-AQ process more financially competitive than the Kraft-Sulfide process, since the Soda-AQ carbonate need not be raised to 1200° C in order to convert sulfate to sulfide.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows a flow chart depicting generally the process of the present invention.

Fig. 2 shows a view of apparatus suitable for practicing the process of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention pertains to a process for the catalytic reduction of heavy oils, kerogens, plastics, bio-masses, sludges and organic wastes to light hydrocarbon liquids, carbon dioxide and amines, all in a single reaction vessel. More particularly, disclosed herein are multiple examples of an improved dendritic process for the reaction of variegate raw materials, and the separation and isolation of the products formed thereby. The invention takes advantage of the reduction in the number of profligate process steps, the cycle time for the reactions, and the capacity to separate the products using a dendritic process. The invention thus directly addresses the need in the art for an improved dendritic process, which is suitable for application in the processing and recycling or disposal of waste from numerous and variable sources, such as, for example, agricultural, industrial and municipal waste products, and including, but not limited to, various wastes that are toxic or potentially hazardous to human or animal health or the environment.

In accordance with the present invention, a pressurized aqueous system is used for the transformation of higher molecular weight organic compounds into lower molecular weight hydrocarbons of reduced viscosity. The invention provides two general methods for reducing the viscosity of organic raw materials. The first is by converting 200-300° C-sensitive esters, thioesters, amides, and amino acids to "one carbon shorter" hydrocarbons and/or amines. The second is by thermolytic cracking of the more labile carbon-carbon and carbon-sulfur bonds at 400-500° C. Separating the lower viscosity constituents from

each other is accomplished by distillation. The combined inorganic phase and metals-tars-organo-sulfur contaminants separation is achieved by centrifugation.

The process of the invention optionally is conducted in batch or continuous fashion, with recycling of unconsumed starting materials, if required or desired. The reaction is conducted in a single reactor zone. The materials of construction employed preferably are inert to the starting materials, intermediate reaction materials, and the final products for the reaction process. The fabrication of the equipment should, of course, be able to withstand the reaction temperatures and pressures.

The invention is suitable as a method for converting organic materials into lower molecular weight hydrocarbons. In a preferred embodiment, this is accomplished by injecting an organic raw material in the form of an aqueous mixture, preferably about 10-50% by weight, through a thin tube (*e.g.*, 1/16 inch). In the preferred embodiment, the amount of water present must be sufficient to provide hydrogen as needed to promote the formation of reduced hydrocarbons. A stirrer in the starting materials reservoir agitates the aqueous mixture of organic raw materials, water and catalyst. A pump that can generate a pressure of 200-250 atmospheres feeds the raw material to the reactor. The pressurized raw material is pre-heated to a minimum temperature of about 250° C, preferably by means of a heat exchanger, before entry into the reactor. The reactor mass is maintained at a temperature of about 400-525° C, preferably about 430-500° C, for example, as predetermined by TGA/MS analysis of the reaction raw material and a pressure that is commensurate with the temperature. A heater (preferably electric) heats the autoclave with the capability to maintain the temperature of the twenty-foot length, sixteenth-inch diameter reactor-tube at approximately 500° C. The system is provided with a cooling coil as it exits the autoclave area. Recovered energy is used to pre-heat fresh raw material as it enters the autoclave reaction chamber. Gas and liquid samples are taken after completion of the reaction and cool down.

Referring now to Figure 2, apparatus suitable for practicing the process of the present invention is shown. Feeding hopper 1 feeds into holding reservoir 2. High pressure pump 3 pumps the raw material into the apparatus, with pressure being monitored by pressure gauge 4. Primary heat exchanger 5 preheats the raw materials. Power control 7 and power supply 8 allow for adjustment of the amount of power delivered to heating coil 6, with temperature meter/controller 9 controlling the temperature. Secondary heat exchanger 10 provides additional heating, as necessary. Back pressure 11 regulates back pressure in the system, and gas/liquid separator allows for removal of gasses or liquids from the system, as necessary. Temperature meter 13 and pressure gauge 14 monitor



temperature and pressure in the system. Gas collection valve 15 allows for the collection of gasses, as necessary, and liquid collection valve 15 allows for the collection of liquids, as necessary. Heat transfer media pump 17 pumps heat transfer media through the system.

The process of our invention teaches that:

- 5 a reaction vessel may contain diverse raw materials in variable proportions, and that the product of one of the reactions may be a catalyst or drying agent for the system as a whole,
- the reactions may be independent or multi-stepped, occurring in concert or cascade fashion,
- 10 the cycle time for the reactions is temperature/pressure dependent and can be controlled in a minimal 3-10 minutes by temperature/pressure regulation in the reaction vessel,
- the temperature at which the reaction vessel is maintained preferably is determined by TGA/MS analysis of the starting materials,
- 15 the reaction products generated during TGA/MS analysis give an indication of the heat levels and time period required for individual reactions,
- the TGA temperature ranges and slopes give a robustness measure of the process variables,
- the array of products formed is isolated by entrapment of the gases, condensation of the liquids in an attached distillation tower, and physical collection of the dry residual solids,
- 20 entrapment of carbon dioxide and amines may be by physical or chemical means, such as physical absorption/adsorption/de-sorption, condensation, crystallization and chemical precipitation,
- 25 entrapment of the amines causes odor abatement,
- through efficient reaction energy recovery and production of a high calorific value product, a net positive energy balance is attained,
- by supplementing very heavy crude with waste animal and/or vegetable oils, a much reduced viscosity and more easily pipelineable mixture is formed,

lipid-supplemented heavy crude constitutes "diverse raw materials in variable proportions" as described in the first point made above,

depending on the aqueous content of the raw material, extra water may or may not be required as solvent, and

no waste products, and hence no environmental footprint, need be left.

Although several specific examples are described in detail below, one skilled in the art will appreciate from the present disclosure that the following examples are merely guides, which are susceptible to substantial modification, and that the invention can process a wide variety of input materials, including mixtures thereof, for numerous different applications. In the various embodiments of the invention described below, the following proportions of components preferably are used.

#### Dendritic Reaction Process

The term "solid entrapment" is intended to refer to bubbling a gas fraction of the reaction mixture first through a lime solution (precipitates calcium carbonate) and then through an acid solution (generates amine salts).

Glycerol is a strong water astringent. Water laden glycerol is hydrocarbon insoluble and forms a separate phase. Distillation of the hydrocarbon phase shows no trace of water present.

#### Example 1 – Continuous Process Mode

A mixture of variegate source triglycerides and lipids (preferably with some protein "contaminant") of animal and/or vegetable origin is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids; hydrolysis of the triglycerides and lipids produces a mixture of C<sub>4</sub> to C<sub>24</sub> carboxylic acids, plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, and C<sub>3</sub> to C<sub>23</sub> hydrocarbons. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. Also optionally, glycerol is added as a desiccant for the generated hydrocarbons and absorbent for the amines. Thus, the dry hydrocarbon phase optionally is separated before fractional distillation is carried out. Hence, in one reaction vessel, water is consumed and a mixture of triglycerides, lipids, and protein is converted to amines, desiccated hydrocarbons, glycerol and carbon dioxide.

In one example, trimmed pork fat, including rind and residual flesh (which is not limiting to the source of animal raw materials that can be used in the process) is pulped. To the pulped fat is added water such that a 50% by weight fat to water mixture is prepared. Pulped pig fat is pumped to the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The pressurized pulp is pre-heated to 250° C by means of a heat exchanger, before entry into the reactor. The reactor is maintained at a temperature of 470° C. Hydrolysis of the triglycerides and proteins with sequential decarboxylation of the freshly generated carboxylic acid functional groups occurs in the twenty-foot length, sixteenth-inch diameter reactor-tube. Generated amine provides a catalytic effect for the hydrolysis reaction and anti corrosive protection of the walls of the reactor. Energy recovered on cooling the exiting autoclave products is used to pre-heat fresh raw material as it enters the autoclave reaction chamber. Gas, liquid and solid products are refined as described above. Skin, ligament and some protein fractions of the pig fat carbonize under the reaction conditions. Physical filtration of the solids from the liquid phases provides solid compost that can be applied to the land as soil builder or burned as a fuel.

#### Example 2- Continuous Process Mode

Animal excrement and vegetable wastes that have a fair proportion of triglycerides, lipids and protein, is subjected to a high temperature in the presence of water, with or without a catalyst. Hydrolysis of the proteins produces a mixture of amino acids; hydrolysis of the triglycerides and lipids produces a mixture of C<sub>4</sub> to C<sub>24</sub> carboxylic acids, plus glycerol. Decarboxylation of the amino acids and the carboxylic acids generate fractionally distillable carbon dioxide, amines, and C<sub>3</sub> to C<sub>23</sub> hydrocarbons, with little, if any, methane gas. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. A higher proportion of protein generates a higher ratio of amines to hydrocarbons. Capture and isolation of the putrid smelling amines provides an odor-free process and nitrogen reduced residue. Solid insoluble coke residue (cellulose derived) and mineral salts also are obtained. Hence, in one reaction vessel, water is consumed and human, swine, or bovine excrement and plant matter are converted to carbon dioxide, amines, hydrocarbons, glycerol, and nitrogen-depleted carbonaceous compost. This odor and pathogen-free residue is suitable for use as a low-grade fuel or compost.

In one example, partially de-watered pig excrement including floor washings (which is not limiting to the amount or type of excrement source that can be used in the process) is prepared as a 20% by weight solids mixture. A pump feeds the conditioned

excrement to the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The pressurized excrement is pre-heated to 250° C by means of a heat exchanger, before entry into the reactor. The reactor is maintained at a temperature of 430° C. Hydrolysis of the triglycerides and proteins with sequential decarboxylation of the freshly generated

5 carboxylic acid functional groups occurs in the twenty-foot length, sixteenth-inch diameter reactor-tube. All pathogenic material is sterilized and becomes part of the raw material. Generated amine provides a catalytic effect for the hydrolysis reaction and anti-corrosive protection of the walls of the reactor. Energy recovered on cooling the exiting autoclave products is used to pre-heat fresh raw material as it enters the autoclave reaction chamber.

10 Gas, liquid and solid products are refined as described in Example 1. The amine fraction is composed of, for example, ammonia from glycine; methyl amine from alanine, aspartic acid, asparagine and  $\beta$ -alanine; dimethyl amine from sarcosine; trimethyl amine from betaine; iso-butyl amine from valine; iso-pentyl amine from leucine; ethanol amine from serine; 1,2-propanol amine from threonine; 1,3-propanol amine from homo-serine;

15 putrescine from lysine, arginine, and ornithine; histamine from histidine; phenethyl amine from phenyl alanine; tyramine from tyrosine; tryptamine from tryptophan; cysteamine from cysteine; pyrrolidine from proline.

Amines are odiferous compounds that are usually associated with excrement and decomposing proteins. Putrescine (1,4-diamino butane) and cadaverine (1,5-diamino

20 pentane) aptly derive their nomenclature from the Latin – putrere or putrefaction and cadere or cadaver. Isolation and containment of the amines is one way to achieve abatement of foul odors.

### Example 3 - Continuous Process Mode

Heavy oils supplemented with waste fats or lipids (as a processing aid in the

25 pipeline transport of crude) are subjected to a high temperature in the presence of SCW. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons thus generates fractionally distillable desiccated lighter hydrocarbons, physically separable water-loaded glycerol, and filterable solids. The solid insoluble residue contains mineral salts and very heavy tars. Hence, in one reaction vessel,

30 water is consumed and lipid-supplemented heavy oil is converted to carbon dioxide, hydrocarbons, and residual organo-sulfur tar contaminant metals.

In one example, 10% by weight waste cooking oil (which is not limiting to the amount or type of triglycerides that can be used in the process) is added to wet crude. The pressurized mixture is pre-heated to 250° C by means of a heat exchanger, before being

pumped into the reactor at a rate of 300 ml/hour under 218 atmospheres of pressure. The reactor is maintained at a temperature of 430° C. Hydrolysis of the triglycerides and tramp proteins with sequential decarboxylation of the freshly generated carboxylic acid functional groups occurs in a twenty-foot length, sixteenth-inch diameter reactor-tube. Generated amine provides a catalytic effect on the hydrolysis reaction. Energy recovered on cooling the exiting autoclave products is used to pre-heat fresh raw material as it enters the autoclave reaction chamber. Gas, liquid and solid products are refined as described above. The distilled hydrocarbon has a boiling range fraction of 60-220° C, which is not present in the starting raw materials.

Experiments were carried out in a batch reactor. The reactor is constructed from a six-inch diameter stainless steel rod of seven-inch length. Eight half-inch diameter bolts are used to hold a cover head in place. A copper gasket is used to maintain an ultimate pressure of 250 atmospheres in the 40 ml volume well of the reactor. Six propane torches are used to heat the reactor to 430-470° C. Ice is used to cool the reactor, once the reaction temperature is reached.

#### Example 4 - Batch Process Mode

Lake Asphalt Tar Sand that has a fair proportion of carboxylic acids is subjected to a high temperature in the presence of super-critical water. Inherent clay catalyst causes decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons, generating fractionally distillable C<sub>12</sub>, plus other hydrocarbons. Solid insoluble residue (mineral salts), and very heavy organo-sulfur contaminated tars also are obtained. Hence, in one reaction vessel, water is consumed and tar sand is converted to carbon dioxide, hydrocarbons, and residual tar-contaminated clay.

In one example, to 40 grams of Trinidadian Lake Asphalt Tar Sand (70% by weight clay) is added 15 ml of water. The mixture is introduced into the reactor and the temperature of the reactor is raised to 430° C. Upon reaching 430° C, the source of heat is shut down and cooling is started. Upon reaching room temperature, the reactor is opened, and trapped carbon dioxide is allowed to escape. The oily-water residual material is extracted with methylene chloride. Distillation of the extract yields a heavy oil that boils above 200° C. The residual clay contains 3% by weight of tar.

#### Example 5 - Batch Process Mode

Heavy oils that have a fair proportion of carboxylic acids are subjected to a high temperature in the presence of SCW, with an iron oxide catalyst or amino acid catalyst,



causing decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons. Fractionally distillable C<sub>13</sub> to C<sub>30</sub> hydrocarbons is generated. Optionally, the use of ash residue from Lake Asphalt Tar Sand as catalyst in the reductive generation of lighter oils from heavy crude causes the separation of metal contaminants and organo-sulfur compounds from the lighter fractions. Solid insoluble residue (mineral salts) containing very heavy tars and organo-sulfur compounds also are obtained. Hence, in one reaction vessel, water is consumed and heavy oil is converted to carbon dioxide, hydrocarbons, and residual tar contaminated clay (in the case of alumina-silica-iron oxide catalyst) or organo-sulfur tar contaminant residual V-Ni-Fe metals (in the case of amino acid catalyst).

In one example, to 20 grams of 57% aqueous butoxyethanol insoluble Athabasca heavy oil (*i.e.*, maltene extracted asphaltene residuum) is added 15 ml of water and 100 mg aspartic acid. The mixture is introduced into the reactor and the temperature of the reactor is raised to 430° C. Upon reaching 430° C, the source of heat is shut down and cooling is started. Upon reaching room temperature, the reactor is opened, and trapped carbon dioxide and ethyl amine are allowed to escape. The oily-water residual material is partitioned using 100 ml 20% by volume butoxyethanol in water at 80° C. All of the viscosity reduced oil dissolves in the top layer (57% butoxyethanol in water) and a solid residue collects at the bottom of the 10% butoxyethanol in water layer.

#### Example 6 - Batch Process Mode

Polyethylene is subjected to a high temperature in the presence of water and iron oxide embedded in an alumina-silica matrix or a basic catalyst, such as sulfide. Reductive thermolytic cleavage of carbon-carbon bonds and oxidation of the sulfide to sulfate ion yields C<sub>22</sub> to C<sub>40</sub> waxes or fractionally distillable C<sub>10</sub> to C<sub>22</sub> hydrocarbons, respectively. Hence, in one reaction vessel, water is consumed and a mixture of hydrocarbons is formed.

In one example, to 20 grams of low density polyethylene film is added 0.5 gm sodium sulfide in 15 ml of water. The mixture is introduced into the reactor and the temperature of the reactor is raised to 460° C. Upon reaching 460° C, the source of heat is shut off and cooling is started. Upon reaching room temperature, the reactor is opened. The oily-water residual material is partitioned from the aqueous phase using 100 ml-methylene chloride. Filtering it through a pad of basic aluminum oxide decolorizes the methylene chloride solution. The kerosene smelling light oil is tested for sulfur content. The water phase is analyzed for sulfide and sulfate content. Performing the reaction using

Lake Asphalt clay residue as catalyst yields a waxy product. The melting point is 25-30° C.

In another embodiment, a mixture of synthetic polymers comprising nylon 6, nylon 6,6, nylon 6,10 and nylon 6,12 is subjected to a high temperature in the presence of SCW, thereby producing a mixture of  $\omega$ -amino caproic acid, 1,6-diamino hexane, hexan-1,6-dioic acid, decan-1,10-dioic acid, and dodecan-1,12-dioic acid. Decarboxylation of the amino acid and the diacids generate fractionally distillable carbon dioxide, plus pentyl amine, 1,6-diamino hexane, butane, octane, and decane. The amines serve as catalysts for these reactions. Other known catalysts, such as acids, bases and iron oxides embedded in an alumina-silica matrix, optionally are added to the reaction vessel for improved performance. Hence, in one reaction vessel, water is consumed and a mixture of four nylon polymers generates two amines, three hydrocarbons and carbon dioxide.

#### Example 7 – Batch Process Mode

Albert shale from Stoney Creek, New Brunswick is subjected to a high temperature in the presence of SCW. Reductive thermolytic cleavage of carbon-carbon bonds yields C<sub>12</sub> to C<sub>26</sub> hydrocarbons, as determined by GC/MS.

In one example, to 25 grams of crushed Albert Shale (20% organic content) is added 10 ml of water. The temperature of the reactor is raised to 460° C. Upon reaching 460° C, the source of heat is shut down and cooling is started. Upon reaching room temperature, the reactor is opened. The oily-water residual material is partitioned from the aqueous phase using 100 ml methylene chloride. Oil is obtained upon evaporation of the solvent. GC/MS analysis indicates that the oil is composed of C<sub>12</sub> to C<sub>26</sub> saturated hydrocarbon.

#### Example 8 – Batch Process Mode

Extracted lignin or black liquor from the Kraft (sulfide plus carbonate) and Soda-AQ (carbonate) process are subjected to super-critical temperatures. Hydrolysis of the esters, decarboxylation of the acids and reductive cleavage of high molecular weight hydrocarbons generates fractionally distillable hydrocarbons and physically separable precipitated carbonaceous solids. The separated aqueous fraction from the Kraft process contains a mixture of carbonate and sulfate ion, but no substantial sulfide ion. Hence, in one reaction vessel, water is consumed and pulp black liquor is converted to carbon dioxide, hydrocarbons, carbonaceous fuel and green liquor, without resorting to an energy intensive five stage evaporation in order to concentrate the black liquor. This makes the

environmentally more friendly Soda-AQ process more financially competitive than the Kraft-Sulfide process, since the Soda-AQ carbonate need not be raised to 1200° C in order to convert sulfate to sulfide.

In one example, 35 ml of 18% Kraft black liquor (sulfide-soda) is placed in the reactor well. The temperature of the reactor is raised to 430° C. Upon reaching 430° C, the source of heat is shut down and cooling is started. Upon reaching room temperature, the reactor is opened. The oily-water residual material is partitioned from a solid phase using 100 ml methylene chloride. Viscous oil is obtained upon evaporation of the dried methylene chloride solvent. GC/MS analysis indicates that the oil is composed mostly of polyaromatic material. Solid powered carbonaceous material is filtered from the reaction mixture. Examination of the water shows that all of the sulfide ions are oxidized to sulfate ions, and that most of the lignin reaction products are precipitated out. Upon standing, the water white aqueous phase begins to take on a brown color, most likely due to oxidation of the water-soluble phenolics. Treatment of 18% Soda-AQ black liquor under the same conditions gives a greater yield of lower boiling point range hydrocarbon and a slightly lesser yield of carbonaceous material.

Several advantages of the invention are listed below in Table 2.

**Table 2:**

1.	Simplicity of the equipment and the process requiring fewer personnel	Low capital costs, maintenance fees and salaries
2.	One step dendritic separation of the organic, water soluble and solid inorganic constituents	Smaller portable reactors with short cycle times
3.	Performing the reaction and separation of constituents in one step	Eliminating the costs of profligate process steps
4.	Can use readily available, diverse mixed-source raw materials	Security against availability of raw materials sources and prices
5.	Reduction in the viscosity of the heavier oil fractions	Increased pipeline flow capabilities at lower temperatures
6.	Up-grading the constituents by concentrating metals into fewer product streams	Reduction of the oil volumes which require de-contamination treatment

7.	Reducing odor producing organosulfur and nitrogen compound products	Eliminates catalyst poisoning; Lowers treatment costs, increases social acceptance
8.	Increases liquid volume yield	Decreases coke yield
9.	Provides a drying agent when glycerol is generated	Eliminates emulsion formation
10.	Reduces the energy cost to delignify cellulose pulps; raises the cost competitiveness of the Soda-AQ process	Provides an alternate recovery method for green liquor in paper making
11.	Uses wastes as a raw material source and leaves no environmental footprint	Eliminates wastes, including pathogenic organisms

Accordingly, it is to be understood that the embodiments of the invention herein described are merely illustrative of the application of the principles of the invention. Reference herein to details of the illustrated embodiments is not intended to limit the scope of the claims, which themselves recite those features regarded as essential to the invention.